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HYDROGEN-ION CONCENTRATION AND WATER SUPPLY PROBLEMS

By Frank Hannan[1]

In view of the increasing interest in the subject of hydrogen-ion concentration, and the growing realization of its importance in water filtration, a brief discussion of some of its aspects may not be out of place at this time.

The first essential is, of course, to grasp the nature of the ambiguity of "alkalinity" (or "acidity") as applied to water, analogous to that of "heat." The heat in the ocean is a quantity of vast magnitude; that in, say, a boiling tea-kettle, is by comparison, absolutely infinitesimal; and yet, the kettle is hotter. Similarly almost all natural waters have a more or less considerable "alkalinity;" but a large percentage of them, if tested with phenolphthalein, for example, will not react alkaline. Hydrogen-ion concentration has the same kind of bearing on problems of "alkalinity" that temperature has on heat problems; or, to take another example, potential difference on electrical problems. This distinction between hydrogen-ion concentration and titratable alkalinity—involving the fact that neither is expressible in terms of the other alone—is fundamental.

In most waters, titratable alkalinity is just bicarbonate content, but if any other hydrolysable anion is present, it will be included. The hydrogen-ions of natural water are for the most part furnished by carbonic acid. Hydroxyl-ions are present from the hydrolysis and the actual hydrogen-ion concentration is the resultant of these two factors. If, for simplicity, we neglect for the moment the neutral salts of strong acids almost always present in natural water, and their influence on the hydrolysis, we can put the matter succinctly in this way; titratable alkalinity is the total concentration of hydrolysable anions while the hydrogen-ion concentration is the degree of hydrolysis permitted by the concentration of weak acid momentarily prevailing. The paradoxical fact that the control of the hydrogen-ion concentration is, in general, exercised by the weak acid—and that in the so-called "weakness" of the acid resides this power—is rather important and is sometimes overlooked.

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The papers of Dr. Massink and Dr. Heymann (1) on the hydrogen-ion concentration of the waters of Holland are a fine introductory study. The conception of "aggressive CO_2" is given great prominence. By this is meant the excess of free CO_2 present over and above the concentration necessary, in equilibrium with the bicarbonate anions, to keep the calcium present from separating out as calcium carbonate. This aggressiveness or non-aggressiveness therefore is only directly applicable to calcium carbonate. Indirectly, however, it has this most important bearing on the behaviour of a water in contact with metallic surfaces, that when the CO_2 concentration lies below the aggressive point, the water will tend to deposit a protective coating of calcium carbonate; while, when it is over the aggressive point, the protecting layer will be dissolved and the metal left open to attack. The highly corrosive character of some of the waters of Holland, as, for instance, Amsterdam (Westerveld), Enschede, Maastricht, Venlo, Wageningen, is probably the practical reason for the particular stress laid on aggressiveness.

Hydrogen-ion concentration is, of course, only one of a number of factors which decide the course of the attack on metals. To get the proper perspective for the varying weights of the several factors, according to whether the vulnerable point taken is (a) service pipes of lead, or (b) boilers, or (c) service pipes etc. of iron, many authorities must be consulted. For lead, recent papers of importance are Liverseege and Knapp (2), Weston (3), and Thresh (4). For boilers, Kestner (5) and Brühns (6). The experiments of Bosshard and Pfenniger (7) are fairly conclusive that in the absence of oxygen, carbonic acid, and electrolyte, corrosion is greatly restricted; that hydroxyl ion, as is well understood, has powerful protecting influence; and that of the commonly occurring ions, Mg^{++} and Cl^- seem the least desirable. Important as the action of water on lead and on boilers is, it is yet far outweighed for most water works by the action exerted on iron at ordinary temperatures. This has been so fully treated recently by Richardson (8) that the last word would seem to have been said. Nevertheless, Dr. Friend (9) has turned a flood of new light on the mechanism of corrosion. Such baffling facts as that sea-water shows greater corrosiveness than fresh water at 10°C., and lesser than fresh at 30°C.; that there is a rapid increase in the corrosiveness of moving water containing dissolved oxygen with the velocity up to a certain maximum, and that it subsequently declines until, at about 5 miles per hour, the corrosion becomes almost negligible, are satisfactorily accounted for. An illustration of the influence of varying velocity may sometimes be observed on examining a bend of considerable diameter through which the flow has been fairly constant. The outside curvature where velocity is high exhibits little or no corrosion, while the inside may show a considerable amount. The simple addition to theory made by Dr. Friend may be summed up in two points. (1) Regard must be had to those properties of iron hydroxides which have come to be known as "colloidal" and (2) the importance of catalytic activity. From the viewpoint of this discussion, the fact deserving attention is that hydrogen-ion concentration exerts considerable influence on the mechanism of colloidal and catalytic systems. It it highly probable that Dr. Friend's theory will furnish a satisfactory explanation, not only of the peculiar and intensive corrosiveness of aluminum sulphate solutions, but also of the known promotive influence of alumina on iron oxide growths. Ackermann's (10) description of the forms assumed by rust growths acquires added interest in the light of Dr. Friend's theory. The strong attractive forces on the surface of the alumina particles form the basis of mechanical filtration. The very thin, firmly adherent, coating of alumina, which results from contact with water carrying alumina hydrosols, may not be an altogether negligible factor where corrosion is concerned. If this be the case—as seems not unlikely—mechanical filtration plants have an added reason to guard against that condition of aggressive CO_2, which will deprive them of the protection afforded by calcium carbonate deposit.

The practical value of the Tillmans curve and table—to be found in Dr. Massink's paper—is therefore considerable. Inasmuch as the data of Tillmans are those of calcium, the metal of greatest consequence for water chemistry, when notable concentrations of certain other cations, chiefly magnesium and iron, are present, the true aggressive point does not lie exactly on the Tillmans curve, as Noll (11), Rodt (12), and Kolthoff (13) point out, Some corrections are necessary for such waters.

The operation of the law of mass-action causes a relation to hold between the respective ion-concentrations of hydrogen and bicarbonate on the one hand, and, on the other, the concentration of either free carbonic acid (the usual condition) or carbonate ion.

When values have been assigned, to any two of the three, the third is also fixed. Dr. Heymann clearly explains this, and shows how the calculation is in general a simple matter. Much the same lines are followed by Greenfield and Baker (15). Unless some simplifying assumptions are made, however, the calculations become complicated. Washburn (16) develops 28 equations for the system CO_2 water, and one univalent base.

While the papers hitherto mentioned give a fairly complete picture of the equilibrium conditions in the system *calcite-carbonic acid-water*, the system *water-carbonic acid-atmospheric air* has received less consideration. It is of equal importance with the former system in arriving at the final equilibrium in any given case, and for purposes of hydrogen-ion control, it is possibly of greater importance.

The classical papers of Dr. Johnston (17, 18) and Johnston and Williamson (19) cover both systems fully and clearly with a wealth of important references. These papers put one in possession of all the important factors.

The work of Wells on carbonic acid will be found illuminating, as, for instance on Gulf water (20) and on Searles Lake (21).

Those desirous of making the hydrogen-ion determination cannot do better than read Dr. Mansfield Clark's (22) invaluable book. The sensitiveness of the hydrogen-ion concentration of natural water to its surroundings—as, for example, in the constant interchange of CO_2 with the atmosphere, in the alkali taken up from glass containers, its reaction to temperature changes, to products of biological activity, and so on, introduces a certain amount of difficulty. The divergence of opinion between the two Dutch chemists, one of whom, Dr. Heymann, prefers the colorimetric method, while the other prefers the direct method, is noteworthy. Dr. Heymann's work is all on the Amsterdam waters, while Dr. Massink's covers the whole of Holland. It is not unlikely that opinion here may exhibit a similar divergence, according as the range of waters under study is narrow or wide. It is interesting to note that Kolthoff (23) leans strongly towards the colorimetric method for water analysis.

The intimate relationship between the chemistry of natural waters and that of soils crops up again and again in the papers of the Dutch chemists. Our waters are, in effect, dilute soil solutions. Furthermore our sands themselves are species of soil. It is well known that there is an active exchange of cations between a soil and a salt solution in contact with it, and that hydrogen-ions frequently take part in the exchange, and, in general, pass from soil to water; athough sometimes the reverse may occur. It is to be expected that reactions of this nature will occur in water filtration. They are probably however, so far as hydrogen-ion concentration is concerned, often outweighed in importance by the changes wrought by the high concentrations of microörganisms. Dr. Heymann on this point is instructive.

The conception of thermal optima, thermal inhibition, and thermal death-points, for the different species of microörganisms, is well-known. The same applies to enzymes, if we substitute for death, irreversible inactivation. For a given species or a given enzyme these thermal points are fairly sharply defined. In many cases the presence of "protective" substances, or other changes in the environment, may give rise to a corresponding change in the thermal point. In just the same way there appear to be for each species and each enzyme, points or zones of hydrogen-ion concentration corresponding to optimum activity, partial inactivation, and death (or total irreversible inactivation). There is this difference between heat and hydrogen-ion, that with the latter, both the upper and lower death point is tolerably sharp, and the range between the two comparatively small: while, in the case of heat, the lower death point seems rather indefinite.

As an example of the bearing of this on water filtration, the hydrogen-ion concentration of many natural waters must fall in the warmer months to a level distinctly restrictive to B. Coli (Chambers (24)).

The high degree of sensitiveness exhibited by living matter towards the hydrogen-ion concentration of the environment is not so very surprising when one considers that a contact between two systems of different hydrogen-ion concentration is tantamount to a difference of electric potential, according to the well-known formula:

$$\text{E.M.F.} = 0.059 \log \frac{C}{C'}$$

where $\log \frac{C}{C'}$, is simply the difference between the pH values of the two systems; and is as great, for example, for a pair of systems pH = 5 and pH = 6—both nearly neutral—as it is for a pair pH = 0, pH = 1, i.e., normal and decinormal. Just as it has been found convenient in the practical application of electricity to construct lamps, motors, etc., to work at a definite range of voltage, and regulate the current to suit, so, it would appear, in nature, is each cell designed to function at its own particular voltage, and supplied with automatic regulators in the form of buffer systems, etc.

In conclusion it may be pointed out that probably the most fruitful application to water filtration will be found in wise wielding of the power thereby placed in our hands to vary the electrical charges on particles of all kinds in the water, from the finest colloid dispersion to the coarsest sand, rendering them, to an extent which even yet seems little realized, more amenable to effective treatment.

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